

A More Benign and Effective SCF Solvent System for Producing Mesophase Pitch

1. Foreword

Although researchers at Clemson are successfully using supercritical toluene as a solvent for the production of mesophase pitches from raw petroleum pitch, the use of solvents that are less hazardous than toluene is always of interest. In addition, a different solvent could in principle be used to modify the chemical characteristics of the mesophase pitch fractions being obtained. The idea of using an aqueous supercritical fluid (SCF) to fractionate petroleum pitches originated from M. C. Thies' interaction with two scientists in Germany. In 1993, E. Brunner of BASF discussed with Thies the results of recent experiments in his laboratory, in which he found that polynuclear aromatic compounds containing up to four aromatic rings become completely miscible in compressed, near critical liquid water [1]. This idea was subsequently tested on a more practical scale by G. Brunner of the Technical University of Hamburg-Harburg, who in collaboration with M.C. Thies demonstrated that pitches and asphalts could be dissolved in near critical water.

Therefore, this exploratory study was undertaken to investigate the influence of adding water to the supercritical toluene solvent system currently used at Clemson for the fractionation of petroleum pitch. The expectation was that the mesophase pitch precursor for pitch-based carbon fibers and carbon-carbon composites could be made by a more environmentally acceptable method.

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13. ABSTRACT (Maximum 200 words) The goal of this study was to investigate the use of more benign solvents, in particular both toluene-water mixtures and neat water, for producing mesophase pitches. Extraction operating conditions of 340 °C and 200 bar were selected such that toluene and water would form a homogeneous, dense supercritical phase. An overall solvent-to-pitch (S/P) ratio of 3.0 was selected for this work, with the solvent compositions being varied from 0 to 100 mol % water. The results of our exploratory work can be summarized as follows. Hot, compressed near critical water can be used to dissolve pitches, but only the lower molecular weight fractions of the pitch are readily dissolved. At moderate S/P ratios (e.g., 3:1), the water functions primarily as an antisolvent, as most of the feed pitch simply precipitates out as a bottom phase that does not differ significantly from the feed pitch in composition or molecular weight. To effectively fractionate the feed pitch with neat aqueous solvents, high S/P ratios (e.g., 10:1) would probably be required. On the other hand, the addition of small amounts of water (e.g., 5-10 wt %) to toluene solvent can be used to precipitate pitches with relatively high melting points that contain mesophase.			
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4. Statement of the Problem

At Clemson, a supercritical extraction (SCE) process is used to fractionate raw petroleum pitches. Fractions can be isolated that consist of 100% mesophase; these mesophases serve as excellent starting materials for high-performance carbon fibers [2]. Currently, near critical or supercritical toluene is used as the fractionating agent. However, the use of more benign solvents is always of interest. Although pitches do not dissolve to any appreciable extent in supercritical carbon dioxide, previous work by other researchers had shown that near critical water will dissolve polynuclear aromatic compounds and pitches [1, 3]. The goal of this study, then, was to investigate the use of both toluene-water mixtures and neat water as solvents for fractionating pitches and thus isolating valuable mesophase fractions.

5. Results and Accomplishments

A. Modifications to the Supercritical Extraction Apparatus

The properties of near critical and supercritical water are quite different from those of the organic solvents (e.g., toluene and xylene) that are currently being used to fractionate pitches [4]. Thus, a number of modifications to the apparatus had to be performed before any successful runs with aqueous solvents could be carried out. Furthermore, additional improvements were made to the apparatus to facilitate its operation regardless of the solvent or feedstock being used. All of these changes are described below.

Modification No. 1. A new liquid-level detection technique. When SCE is used to produce mesophase pitch, the separation of the mesophasic and isotropic portions of the pitch occurs in a region of liquid-liquid equilibrium where both phases are black and opaque. Hence, a nonvisual technique must be used to monitor the interface level in the cell, ensuring that cross-contamination of the phases does not occur as they are collected. The interface detection device consists of a stainless steel plate that is inserted into the cell chamber and is then electrically isolated from the rest of the cell with ceramic insulators. A wire is attached to the plate and passed through the cell wall by using an insulated, compression-type electrical fitting that contains a lava seal. When using toluene or xylene as an extractive solvent, the plate serves as one electrode of a parallel-plate capacitor, and the inner chamber of the cell body serves as the other electrode. The wire is connected to one leg of an AC impedance bridge, and a multimeter is used to measure a voltage difference that can be related to the interface level in the cell (see Figure 1).

Unfortunately, this capacitance method does not function properly when the solvent mixture contains water. In essence, the water “shorts out” the capacitor. Fortunately, we discovered that the two liquid phases in the cell have significantly different DC resistances. A resistance method of liquid-level detection was subsequently developed and tested, and was found to be a reliable indicator of interface level for aqueous solvent systems (see Figures 2 and 3). It is interesting to note that the resistance method has been found to be superior to the capacitance method no

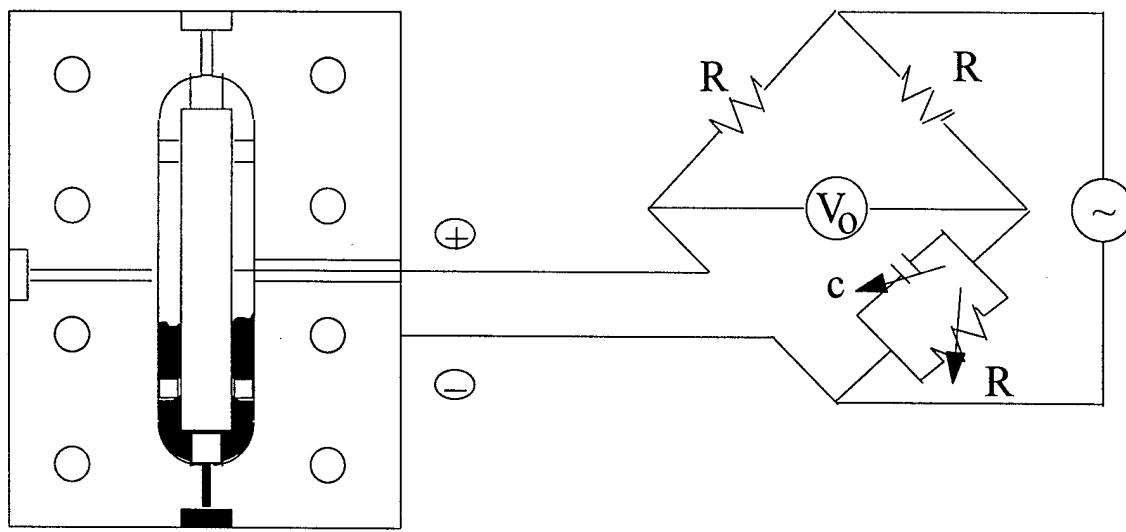


Figure 1. For organic supercritical solvent systems, a capacitance method can be used to detect the liquid-liquid interface level in the cell [5].

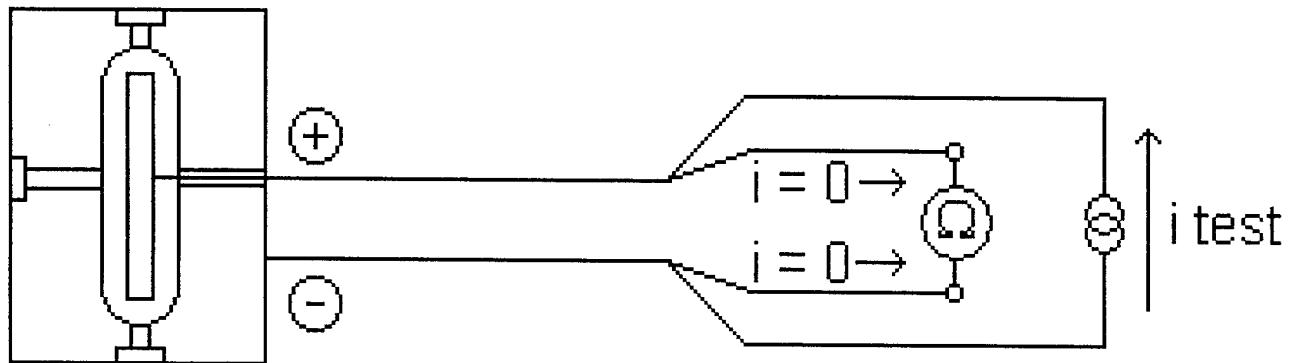


Figure 2. For supercritical solvent systems containing water, a DC resistance method must be used. Because of its superior reliability and durability, this method is now used for both aqueous and organic supercritical solvent systems.

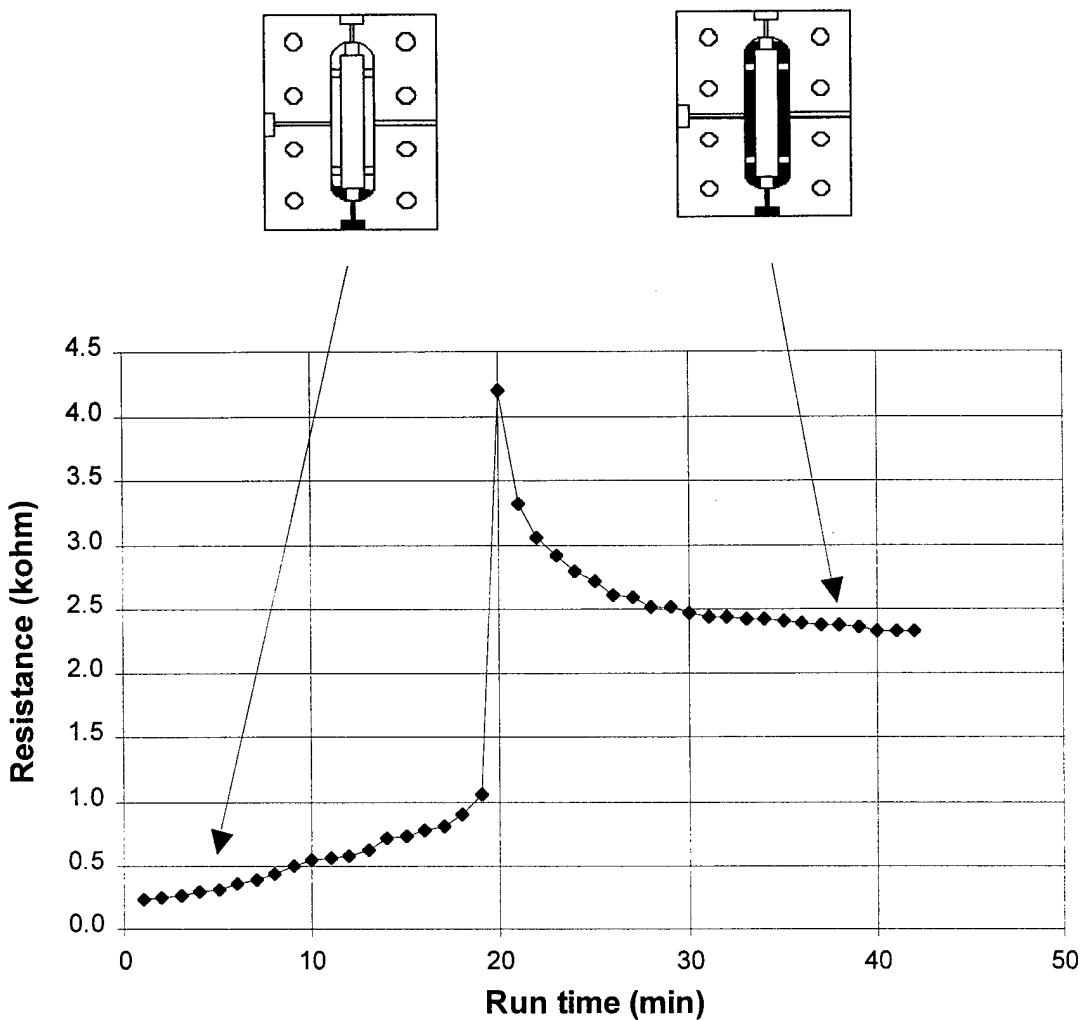


Figure 3. Typical variation of resistance during accumulation of bottom phase in the equilibrium cell. The solvent contains 94.9 mol % (78.4 wt %) water [7].

matter what solvent system is being used! Therefore, we now use DC resistance for liquid-level detection in all of our experiments [6].

Modification No. 2. Improved solvent-refilling system for continuous mesophase production.

When significant amounts of mesophase pitch are being produced (e.g., ≥ 200 g), the solvent reservoir has to be refilled several times during the course of an experimental run. With the original setup, the nitrogen blanket pressure on the feed reservoirs of ~ 30 psi had to be shut off when the reservoir was refilled. Refilling was performed by vacuum pumping, that is, pulling a vacuum on the reservoir and then siphoning solvent into the reservoir. One of the graduate students, Justin Wince, noticed that the refilling procedure for the solvent reservoir was having a measurable effect on the flow rates of the solvent and pitch. Therefore, he designed and

constructed a new refilling system and procedure. In particular, a new solvent reservoir and a system of valves added so that the primary solvent reservoir could be isolated, depressurized, refilled via vacuum pumping, and repressurized while the apparatus was still producing mesophase pitch. As can be seen in Table I, this modification has significantly enhanced the stability of the top- and bottom-phase flow rates. These more stable flow rates have resulted in more reproducible mesophase fractions and fewer unplanned system shutdowns due to, for example, plugs in the lines.

**Table I. Effect of Improvements to Solvent-Refilling System on the Stability of Flow Rates for Mesophase Pitch Production at 320 °C,
1350 psig, S/P Ratio = 3.5 [8]**

Date of Run	Top Phase			Bottom Phase		
	Average Flow Rate, g/h	Standard Deviation	Overall Standard Deviation	Average Flow Rate, g/h	Standard Deviation	Overall Standard Deviation
Before Modification						
10/27/97	713.62	9.21		29.52	1.48	
12/3/97	716.69	9.35	15.09	31.12	1.42	2.39
5/8/98	718.04	9.30		34.63	1.10	
After Modification						
7/29/98	752.06	3.87		36.34	0.39	
8/3/98	750.40	5.48	3.69	35.10	0.09	0.59
8/4/98	753.27	2.00		35.87	0.04	

Modification No. 3: A new computer control system for the apparatus that incorporates Labview. We developed a new control system for the SCF extraction apparatus based on National Instruments' PC-based data acquisition and control system known as Labview. Labview was chosen because (1) much of its hardware and software could be used "as is" on our apparatus, (2) our existing hardware for valve control could be readily incorporated into Labview, (2) Labview uses a graphical programming language that can be readily learned by graduate students, (3) the company provides excellent technical support, and (4) Labview is increasingly used by other researchers at Clemson, which in essence provides "in-house" technical support among graduate students in different departments.

The control system was designed and constructed to control the following components of the SCE apparatus: the system pressure, the phase interface level in the equilibrium cell, and the temperature of the feed and sampling lines. In addition, the new control system monitors temperatures throughout the SCE apparatus and records all necessary data produced during an experiment. Pressure control is accomplished using a PI controller that regulates the pressure by the continuous adjustment of a micrometering valve with a servomotor. Pressure control is maintained to within ± 10 psi during the production of mesophase in the region of liquid-liquid equilibrium. The DC resistance method described under "Modification No. 1" was also incorporated into the Labview scheme. The lines entering and leaving the high-temperature nitrogen bath are maintained to within ± 5 °C of the desired setpoint, which is more than adequate for our purposes. The virtual instrumentation control panel as it appears on the computer monitor is shown in Figure 4, and has a number of useful features. For example, the "cell level" icon tells the operator what the level of mesophase in the cell is at a glance, the "resistance history" chart indicates how well the interface level in the cell is being controlled during the course of a run, and the "pressure history" demonstrates how well the system responds to a desired change in the pressure setpoint.

B. Fractionation of Petroleum Pitch with Aqueous Supercritical Solvents

Once the liquid-level detection device had been modified for aqueous solvents (see "Modification No. 1"), experiments were undertaken to investigate the influence of adding water to the toluene solvent system currently used at Clemson for the fractionation of petroleum pitch. Extraction operating conditions of 340 °C and 200 bar were selected because at these conditions toluene and water form a completely miscible, dense supercritical phase. An overall solvent-to-pitch (S/P) ratio of 3.0 was selected for this work, with the composition of the solvent being varied from 0 to 100 mol % water. For each experimental run, the pitch content of each phase, the softening point of the pitch fraction after drying, and the global product yield were measured or calculated. In addition, selected fractions were analyzed by diffuse reflectance infrared Fourier transform spectroscopy, or DRIFTS.

As shown in Figure 5, the product yield, defined as the fraction of the pitch that precipitates as a bottom phase, increases with increasing amount of water in the solvent. However, even at high (i.e., 80 wt %) water levels, 20% of the pitch is still soluble in the solvent phase. On the other hand, Figure 6 illustrates how the softening point of the higher molecular weight bottom phase drops by more than 100 °C when even 10 wt % of the toluene in the solvent is replaced with water. As the concentration of water continues to increase, the softening points of the top- and bottom-phase fractions approach each other. DRIFTS spectra of these two fractions indicate that this approach in softening point occurs because the top- and bottom-phase fractions are becoming chemically similar to each other in the presence of water.

The results of our exploratory work with aqueous supercritical solvents for the production of mesophase pitches can be summarized as follows. Hot, compressed near critical water can be used to dissolve pitches, but only the lower molecular weight fractions of the pitch are readily dissolved. At moderate S/P ratios (e.g., 3:1), the water functions primarily as an antisolvent, as

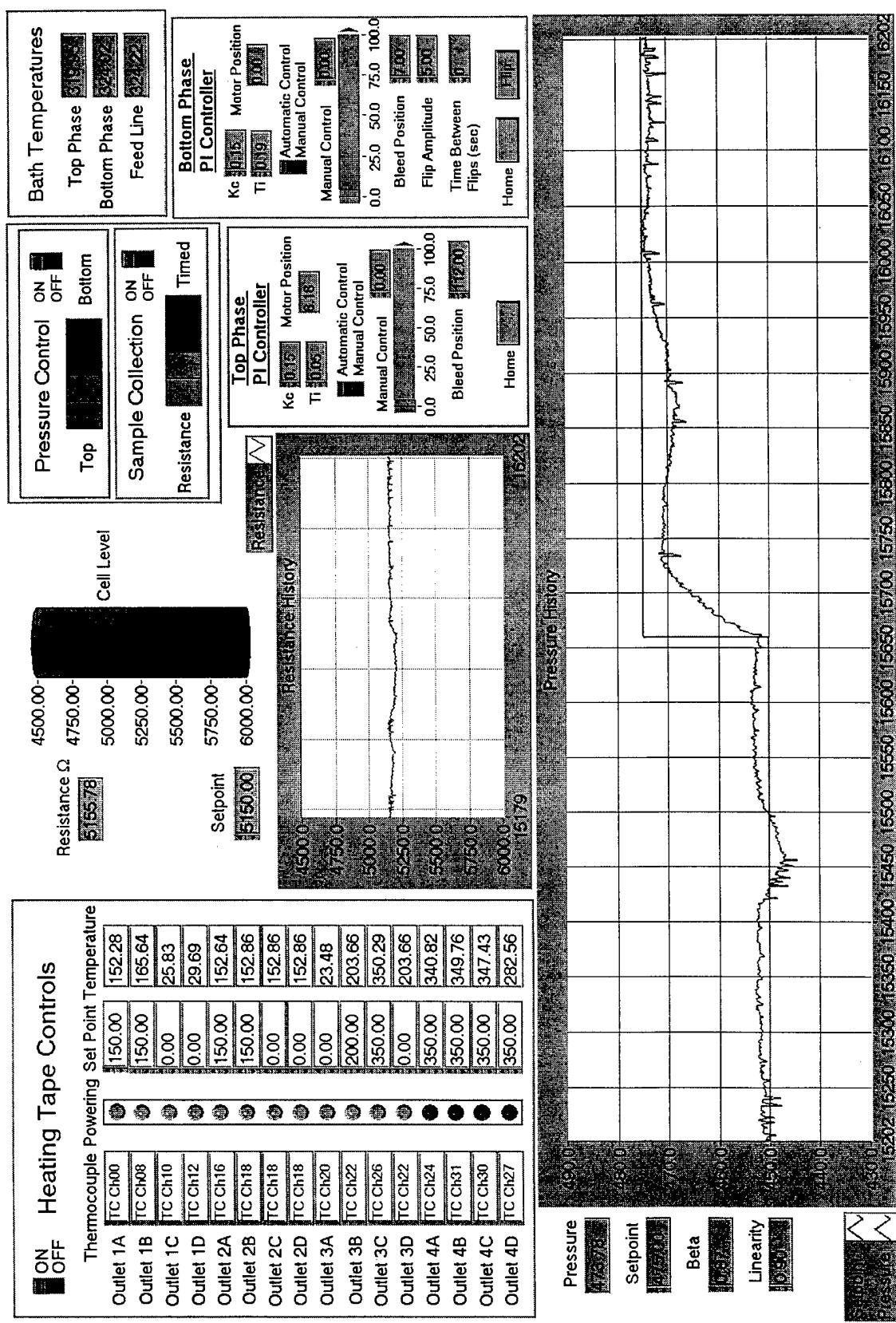


Figure 4. The virtual instrumentation control panel (as it appears on the computer monitor) for the SCE apparatus [8].

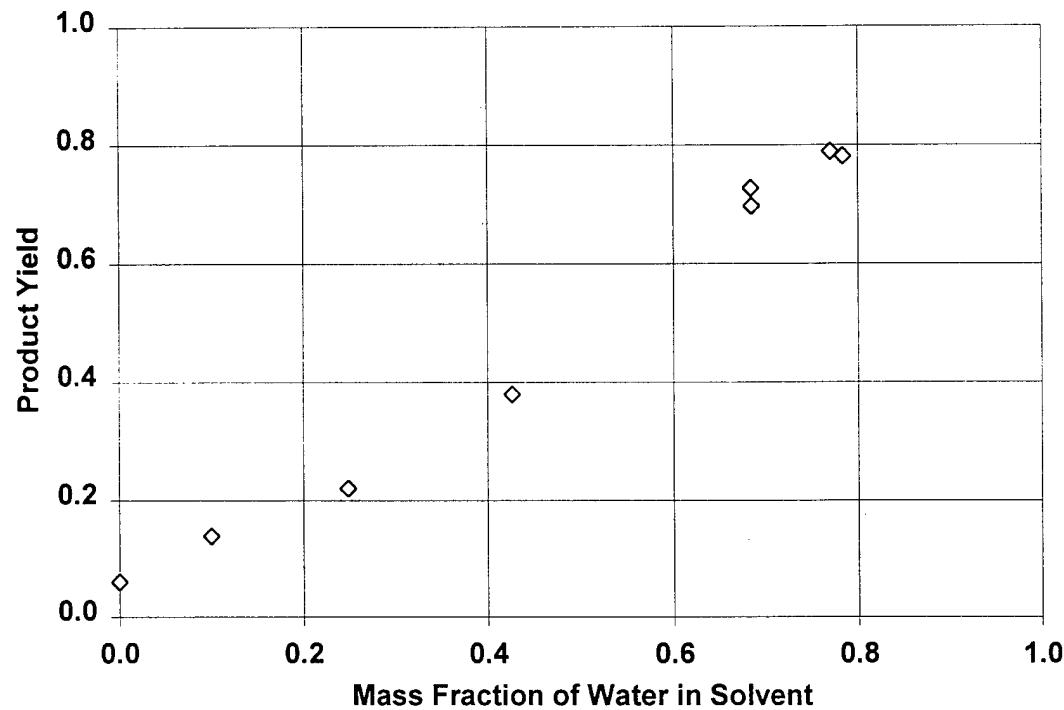


Figure 5. Effect of solvent composition on product yield (the other solvent component is toluene) at 340 °C, 200 bar, and an S/P ratio of 3.0 [7].

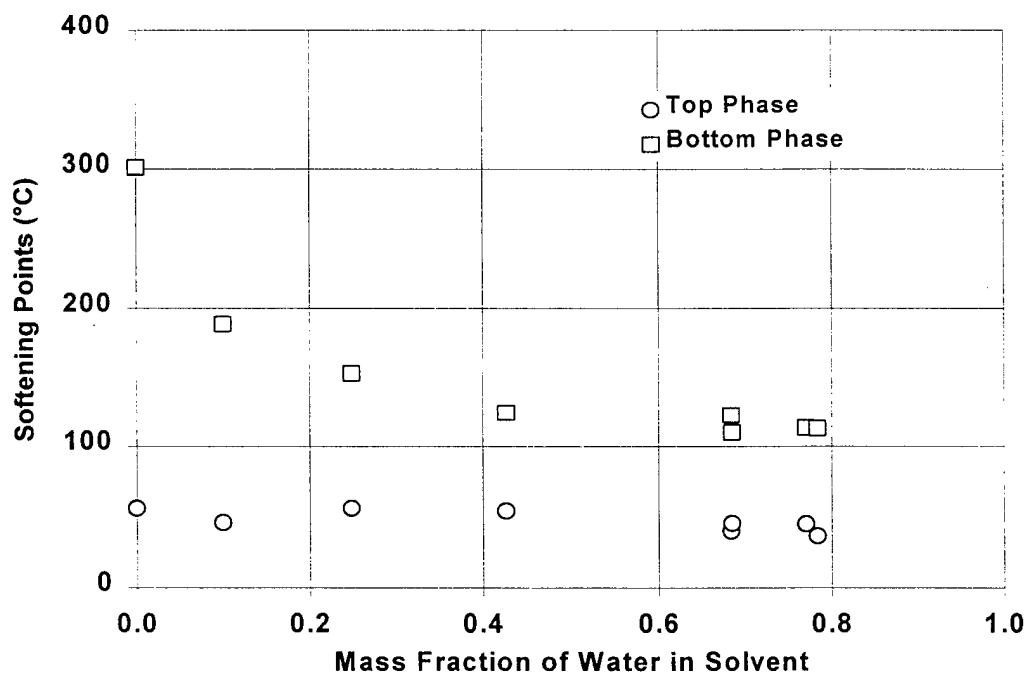


Figure 6. Effect of solvent composition on softening points of top and bottom phases (the other solvent component is water) at 340 °C, 200 bar, and an S/P ratio of 3.0 [7].

most of the feed pitch simply precipitates out as a bottom phase that does not differ significantly from the feed pitch in composition or molecular weight. To effectively fractionate the feed pitch with neat aqueous solvents, high S/P ratios (e.g., 10:1) would probably be required. To test this idea, a new type of experimental apparatus would have to be designed and constructed, and the funds for such work were not available in this one-year, supplemental grant.

Finally, the addition of small amounts of water (e.g., 5-10 wt %) to the toluene solvent can be used to precipitate pitches with relatively high melting points that contain mesophase. However, it is not clear whether the precipitated fractions would differ significantly from those that can be precipitated by a change in the density of supercritical toluene.

6. List of Publications and Technical Reports

Refereed Journals

- a. Zhuang, M. S.; Thies, M. C. Extraction of petroleum pitch with supercritical toluene: experiment and prediction. *Energy Fuels*, in press.
- b. Pigott, R. T.; Wesse, T.; Mullins, J. C.; Thies, M. C. Henry's law constants for solvents in carbonaceous pitches by gas-liquid chromatography. *Ind. Eng. Chem. Res.*, to be submitted for publication, 1999.

Conference Proceedings

- a. Thies, M. C. Processing carbonaceous pitches in dense supercritical fluids: opportunities and challenges (invited plenary lecture). In *Extended Abstracts and Program*, Proceedings of Carbon '99. 24th Biennial Conference on Carbon, Charleston, SC, July 1999; American Carbon Society, 1999; pp 424-426.
- b. Zhuang, M. S. and M. C. Thies, "Fractionation of Petroleum Pitch with Supercritical Toluene", presented at the AIChE 1999 Spring National Meeting, Houston, TX, March 1999, paper 61b.
- c. Wince, J. E., Zhuang, M. S. and M. C. Thies, "Fractionation of Coal Tar and Petroleum Pitches by SCF Extraction", presented at the AIChE 1998 Annual Meeting, Miami Beach, FL, November 1998, paper 141f.

7. List of all Participating Scientific Personnel Supported by this Project

Faculty: M. C. Thies

Ph.D. Students: M. S. Zhuang

M.S. Students: T. Wesse, J. E. Wince

Undergraduate Lab Assistants: J. McLaurin, B. Leggett

Degrees Received While Employed on the Project:

M.S.

1. P. Meinkoehn. Fractionation of Petroleum Pitches with Near Critical and Supercritical Fluids. M.S. Thesis, Clemson University, Clemson, SC, 1997.
2. T. Wesse. Determination of Henry's Law Constants for Solvents in Carbonaceous Pitches by Gas Chromatography. M.S. Thesis, Clemson University, Clemson, SC, 1999.
3. J. E. Wince. Control of a Supercritical Extraction Apparatus Using Virtual Instrumentation. M.S. Thesis, Clemson University, Clemson, SC, 1999.

8. Report of Inventions: None

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6. Zhuang, M. S.; Thies, M. C. Extraction of petroleum pitch with supercritical toluene: experiment and prediction. *Energy Fuels*, in press.
7. P. Meinkoehn. Fractionation of Petroleum Pitches with Near Critical and Supercritical Fluids. M.S. Thesis, Clemson University, Clemson, SC, 1997.
8. J. E. Wince. Control of a Supercritical Extraction Apparatus Using Virtual Instrumentation. M.S. Thesis, Clemson University, Clemson, SC, 1999.